Upper Hudson River PCB Modeling System Overview – PCB Fate and Transport Model

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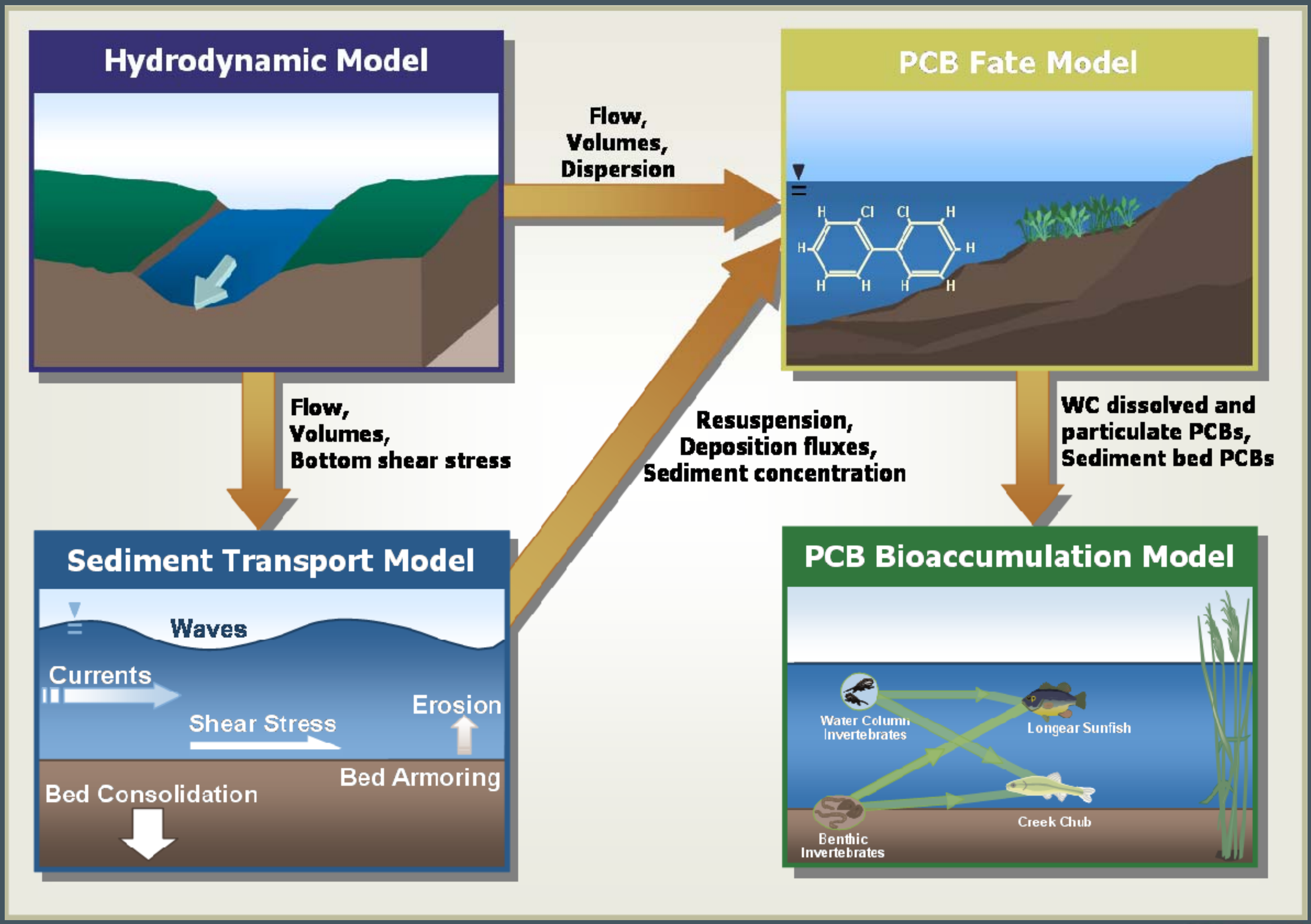
PCB Fate and Transport Model

- Overview of model
  - Processes and theory
  - Structure and parameterizations
  - Assumptions
- Calibration summary
  - Short-term water column calibration
  - Long-term sediment calibration

Model Framework



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What is Modeled?

- Two aggregate PCB species
  - "Di-" ➔ Mono- and di-chlorinated PCBs
  - "Tri+" ➔ PCBs with three or more chlorines
- Note that the 1999 Hudson Model simulated only Tri+, due to data limitations
- Each species is run as a stand-alone simulation
- The fate and transport of each species is modeled in both the water column and the sediment bed

AQFATE Model Code

- Embedded in Anchor QEA’s modified version of EPA’s Environmental Fluid Dynamics Code (EFDC)
- Part of the same general framework as the hydrodynamic and sediment transport models
  - However, Hudson-specific customizations have lead to separate source codes for hydro/sedtran and PCB fate
- Usually run in “external” mode
  - Using stored hydrodynamic and sediment transport output (i.e., linkage via “coupling files”)
  - Improves run-time
- Simulates transport in both the water column and the sediment bed

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PCB Fate Model Structure

- Same model grid as hydrodynamic and sediment transport models
- 2D water column overlies a 3D sediment bed
  - Water column is vertically integrated (i.e., 1 layer)
  - Sediment bed is vertically discretized
    - Ten 1-inch layers (initially)
    - No horizontal transport within bed (only vertical)
  - Separate transport equations for each, linked by the fluxes across the sediment-water interface

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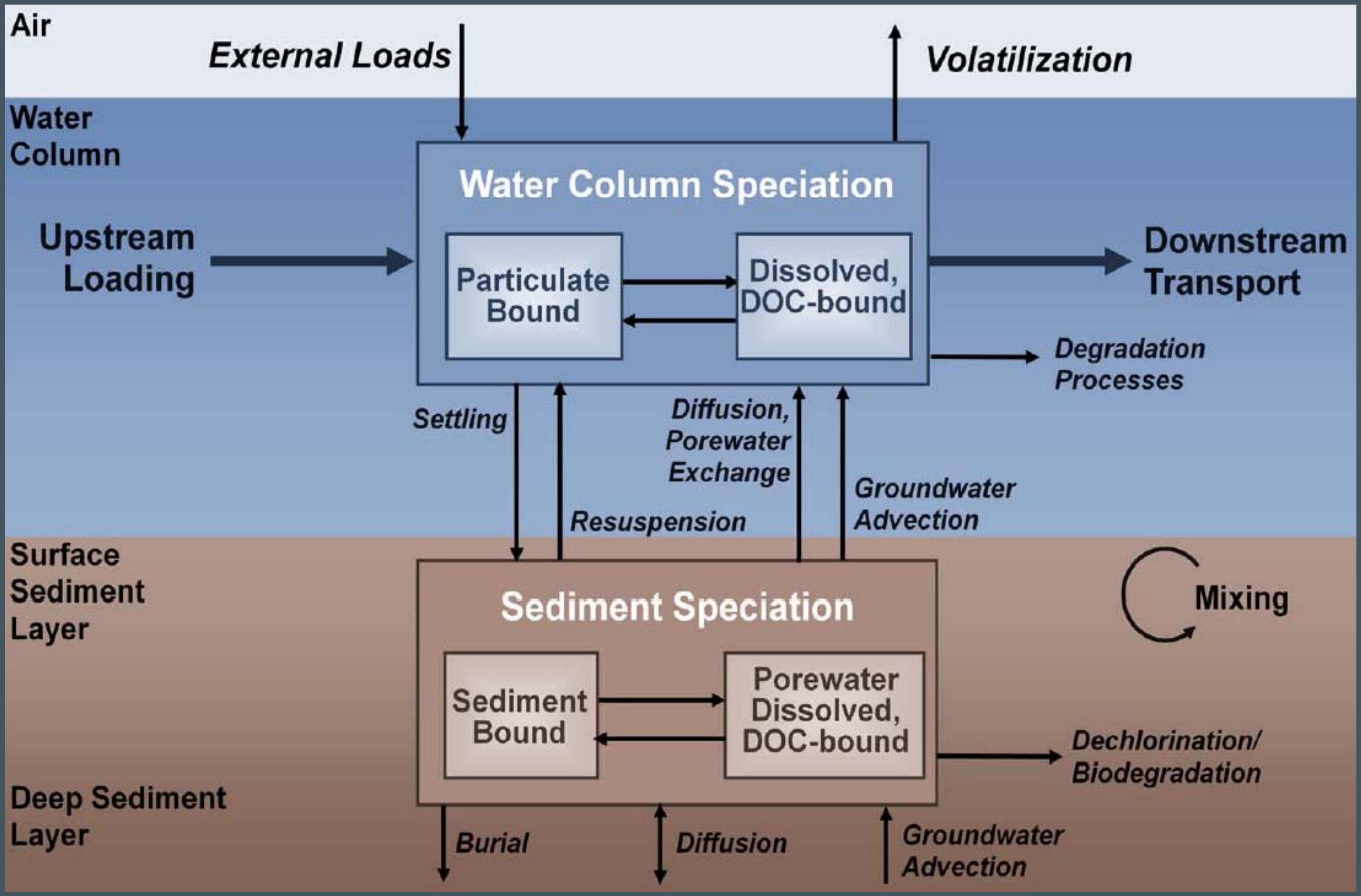
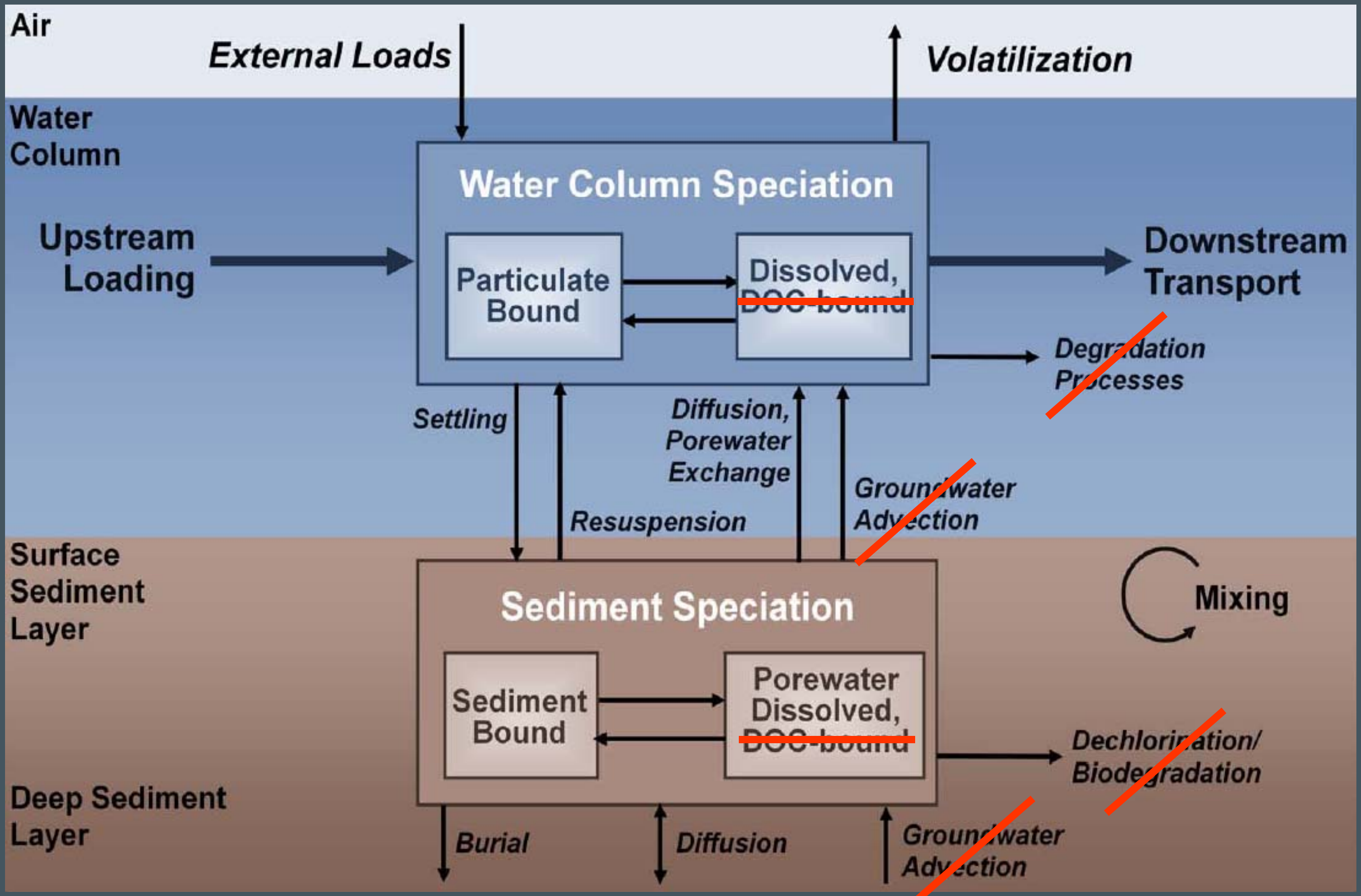
PCB Fate and Transport Processes*



*General description; not all processes are explicitly included in Hudson model

PCB Fate and Transport Processes*



*General description; not all processes are explicitly included in Hudson model

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Equilibrium Partitioning

- Model assumes instantaneous equilibrium partitioning

$$r = K_p c \quad \longrightarrow \quad f_d = \frac{\theta}{\theta + K_p m} \qquad f_p = \frac{K_p m}{\theta + K_p m} \qquad \begin{array}{l} c = f_d c_T \\ p = f_p c_T \end{array}$$

- Consequently, the state variable that the model tracks is total chemical concentration

$$c_T \; (= p + c = f_p c_T + f_d c_T)$$

c_T = total chemical concentration (M/L^3)

c = dissolved chemical concentration (M/L^3)

r = particulate chemical concentration (M/M)

p = particulate chemical concentration (M/L^3)

K_p = partition coefficient (L^3/M)

m = concentration of solids (M/L^3)

f_p = particulate fraction

f_d = dissolved fraction

θ = porosity

Governing Equations

- Transport in water column (2D vertically averaged)

$$\frac{\partial c_T}{\partial t} = \frac{\partial}{\partial x}\left(E_x \frac{\partial c_T}{\partial x}\right) + \frac{\partial}{\partial y}\left(E_y \frac{\partial c_T}{\partial y}\right) - \frac{\partial u_x c_T}{\partial x} - \frac{\partial u_y c_T}{\partial y} - \frac{D_{tot}}{hm}\left(f_p c_T\right) \pm S$$

c_T = total chemical concentration
E = dispersion coefficient**
u = velocity*
D_{tot} = depositional flux of solids*
S = other sources and sinks (e.g., erosion, volatilization, diffusive exchange with sediments)**

h = depth of water column*
m = concentration of solids*
f_p = particulate fraction

**Provided directly by hydrodynamic or sediment transport model output*
***Calculated from hydrodynamic or sediment transport model output*

Governing Equations

- Vertical transport within sediment bed (1D)

$$\frac{\partial c_T}{\partial t} = \frac{\partial}{\partial z}\left(E_p \frac{\partial p}{\partial z}\right) + \frac{\partial}{\partial z}\left[E_d \frac{\partial (c + \cancel{c_{dom}})}{\partial z}\right] - \frac{\partial \cancel{u}_z (c + \cancel{c_{dom}})}{\partial z} \pm S_b$$

c_T = total chemical concentration

c = dissolved chemical concentration

c_{dom} = concentration of chemical bound to DOM (neglected)

E_p = dispersion coefficient (e.g., particle mixing due to bioturbation)

E_d = diffusion coefficient (molecular)

u = groundwater velocity (neglected)

f_p = particulate fraction

S_b = sources and sinks**

(e.g., diffusive exchange with water column, erosion, deposition)

***Calculated from hydrodynamic or sediment transport model output*

PCB Transport Processes

- Advection and diffusion in the water column
- Diffusive transport within sediment bed
- Sediment mixing within bed
- Diffusive transport across sediment-water interface
- Sediment erosion and deposition

Advection and Diffusion in the Water Column

- Calculated using the EFDC scalar transport solver
  - Combines information from hydrodynamic model with PCB source and sink terms (described below) to solve the governing transport equation
  - PCB fate model uses same transport algorithm as the sediment transport model

Diffusive Transport Within the Sediment Bed

- Diffusive flux (*J*) between adjacent sediment bed layers *i* and *j*

$$J_{i,j} = \frac{D_S}{l_{i,j}}\left[(c + \cancel{c}_{dom})_i - (c + \cancel{c}_{dom})_j\right]$$

- Pore-water molecular diffusion coefficient (here D_s)
  - Estimated for each species and corrected for sediment bed porosity (tortuosity)
- Mixing length $l_{i,j}$ taken as the thickness of bed layers (1")

PCB Flux Associated with Sediment Mixing

- Analogous to diffusive mass transport, but
  - Applied to particulate fraction, rather than dissolved
  - Particle mixing (or dispersion) coefficient is a property of the sediment bed and biological activity within, not the chemical species
- Key parameters: depth and intensity of particle mixing
  - Treated here as calibration parameters, guided by literature values
- Combined transport via sediment mixing and molecular diffusion handled by the bed sub-model, along with PCB source/sinks to top sediment layer

Diffusive Transport Across the Sediment-Water Interface

- Transfer of PCBs between sediment porewater and water column

$$J_D = k_f[(c + \cancel{c_{dom}})_s - (c + \cancel{c_{dom}})_w]$$

- Constitutes either a concurrent sink to top sediment bed layer and source to water column, or vice versa
- Magnitude of exchange specified by a sediment-water mass transfer coefficient, k_f
  - K_f represents combined effect of multiple processes

Diffusive Transport Across the Sediment-Water Interface

- Multiple mechanisms may contribute to k_f
  - Molecular diffusion
  - Transport of collodial material
  - Groundwater advection
  - Bioturbation
  - Bottom roughness-induced exchange
- Estimated from the observed increases in PCB concentration across the Thompson Island Pool (TIP, Reach 8) during low to moderate flows

Estimation of k_f

- Used 2004-2008 BMP data to calculate k_f for Reach 8 for Di- and Tri+ independently:

$$k_f = \frac{Q_{FE}\left(C_{T_{TID}} - C_{T_{RI}}\right)}{A_S(C + C_{dom})_s}$$

- Resulting dataset exhibited both flow and seasonal dependence
- We derived seasonally variable functions which relate k_f to the flow at Fort Edward
  - Allows for k_f to be specified using daily flow data

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Estimation of k_f

Formally, let:

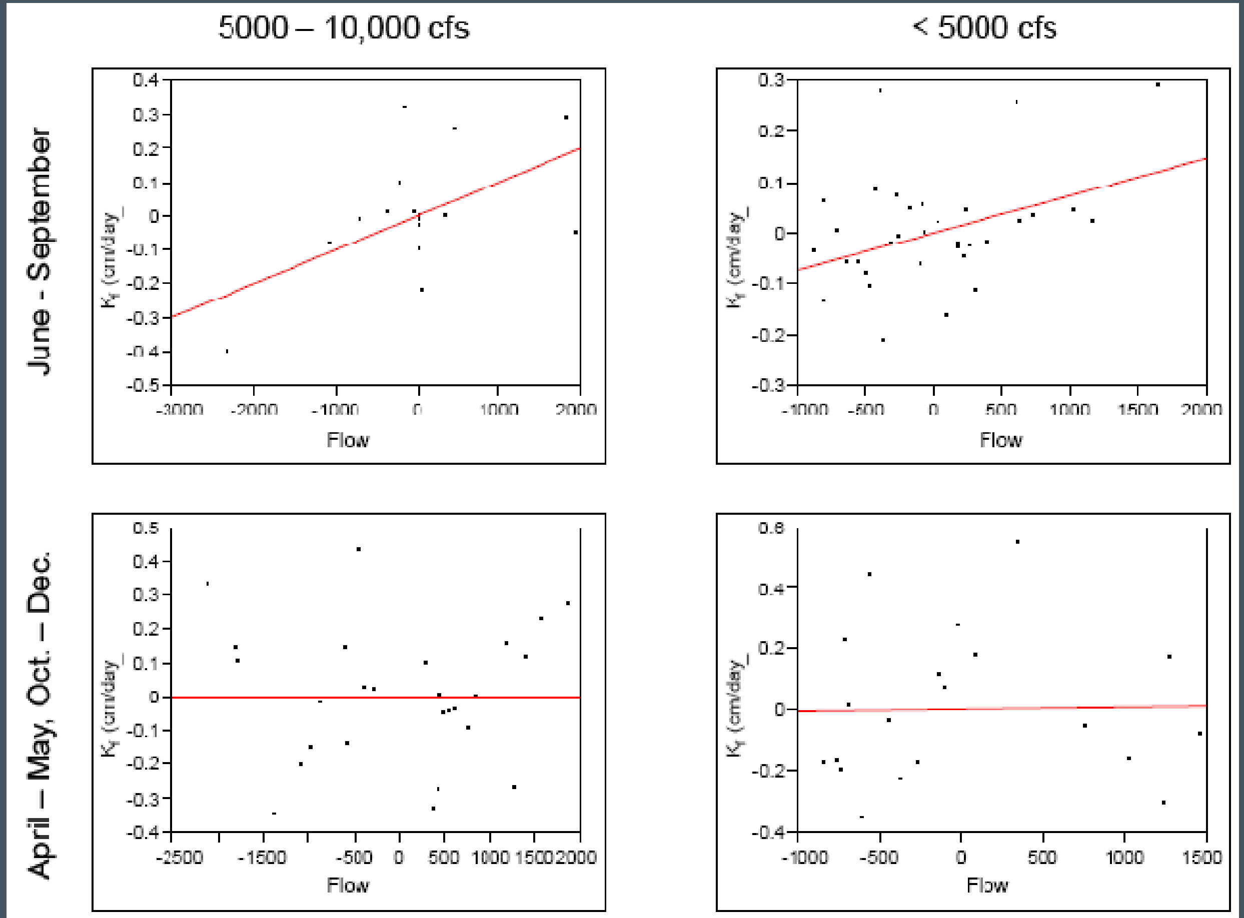
$K_f = \langle K_f \rangle + K_f'$

$Q = \langle Q \rangle + Q'$

Assume:

$\langle K_f \rangle = f(t)$

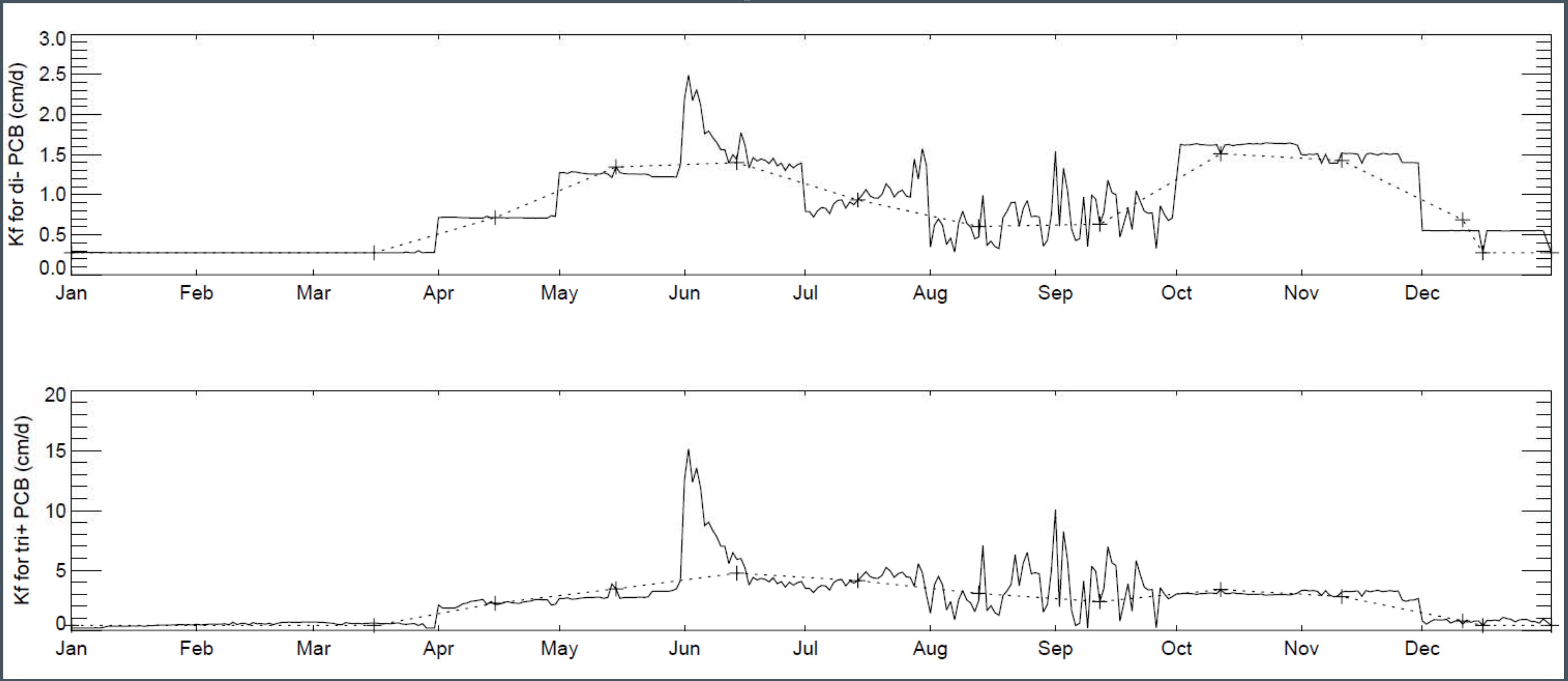
$K_f' = f(Q')$



Note:
Least square regression lines indicate trend in deviation from the mean vs. flow in high flow (5000 – 10,000 cfs) and low flow (<5000 cfs) during warm and cold months.

K_f held constant above 10,000 cfs

Example of Model k_f Inputs



Sediment-water Mass Transfer Coefficients Used in Calibration Simulations, Year 2004

Solid line represents calculated daily k_f values; dashed line represents an interpolation of monthly average k_f values calculated from the data

PCB Flux via Sediment Erosion and Deposition

- PCB fluxes calculated by combining sediment fluxes with predicted PCB conc. on particles
  - Depositional flux
    - PCB source to the top sediment bed layer and sink to water column
    - Concentrations from equilibrium partitioning in the water column
  - Erosion flux
    - PCB sink to the top sediment bed layer and source to water column
    - Concentrations from equilibrium partitioning in the sediment bed

PCB Flux via Sediment Erosion and Deposition

- Erosional flux adjusted to account for resistantly sorbed PCB phase in an approximate manner
  - During calibration, chemical erosion flux of sediment classes 2, 3, and 4 was reduced by 50%
    - Past studies suggest that ~50% of sediment-bound PCBs desorb on timescales > 1 week (e.g., Carroll 1994)
  - Represents PCB phase with desorption timescales much greater than average resuspension time of coarser particles size classes (~1 to 3 hours or less)
- Will be discussed further in context of calibration results

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PCB Transfer and Reaction Processes

- Adsorption
- Volatilization
- Dechlorination/Biodegradation

Adsorption – K_{oc} Values

- Partitioning in sediments
  - Tri+ $K_{oc} = 10^{5.55}$
  - Di- $K_{oc} = 10^{4.72}$
  - Based on 1991 GE sampling program measurements of porewater concentration
- Partitioning in water column
  - Tri+ $K_{oc} = 10^{5.65}$
  - Di- $K_{oc} = 10^{4.74}$
  - Based on 1995 USEPA Phase 2 water column data
- Temperature dependent effects included for both (see report for details)

Volatilization

- Rate of volatilization depends on
  - Mass transfer coefficient at air-water interface
  - Freely dissolved PCB concentrations in the water column
  - Henry's Law "constants"
    - Estimated from data from Brunner et al. (1990) for each species
- PCB sink due to volatilization

$$S_v = \frac{k_L}{h}\left(c - \frac{\cancel{c_{air}}}{H}\right)$$

Volatilization

- Mass transfer modeled via standard two-film theory

$$k_L = \frac{k_g k_l}{k_g + \frac{k_l}{H}}$$

- For PCBs, overall transfer dominated by liquid film transfer, k_l, which was specified via the velocity-dependent O'Connor Dobbins equation

$$k_l = \sqrt{\frac{D_W U}{h}}$$

- Temperature dependence of k_l was approximated via an Arrhenius equation (see report for details)

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Dechlorination / Biodegradation

- Loss of Tri+ PCBs due to dechlorination and concurrent gain of Di- PCBs was not simulated
  - Post-1977 dechlorination assumed to have an minor impact on Tri+ concentrations within sediment deposited prior to 1977
  - Sediments deposited after 1977 are relatively low (~1 to 50 ppm), which may impede dechlorination
    - Based upon the observed relationship between dechlorination rate and total PCB concentration
  - See report for details
- Di- PCB also assumed negligible

PCB Fate Model Calibration

- Two calibration periods
  - 1/1/2004 to 12/31/2008
    - All 8 reaches
    - Semantics: “the calibration”
  - 5/1/1977 to 12/31/2003
    - Reach 8 only
    - Semantics: “the long-term calibration”
- Approach
  - 2004 to 2008 period was used to calibrate model’s prediction of water column trends
  - 1977 to 2003 period was used to calibrate model’s prediction of sediment trends

Model Setup for Water Column Calibration

- Initial conditions
  - Sediment PCB concentrations
  - Bed properties (static)*
  - Suspended particle properties (static)*
- Temperature (cyclic)*
- Boundary conditions
  - PCB loads

These apply to long-term calibration period as well, but will be discussed here

Initial Conditions

- PCB concentrations
  - PCB data from SSAP cores
  - Tri+ concentrations determined from Tri+ to Aroclor correlation

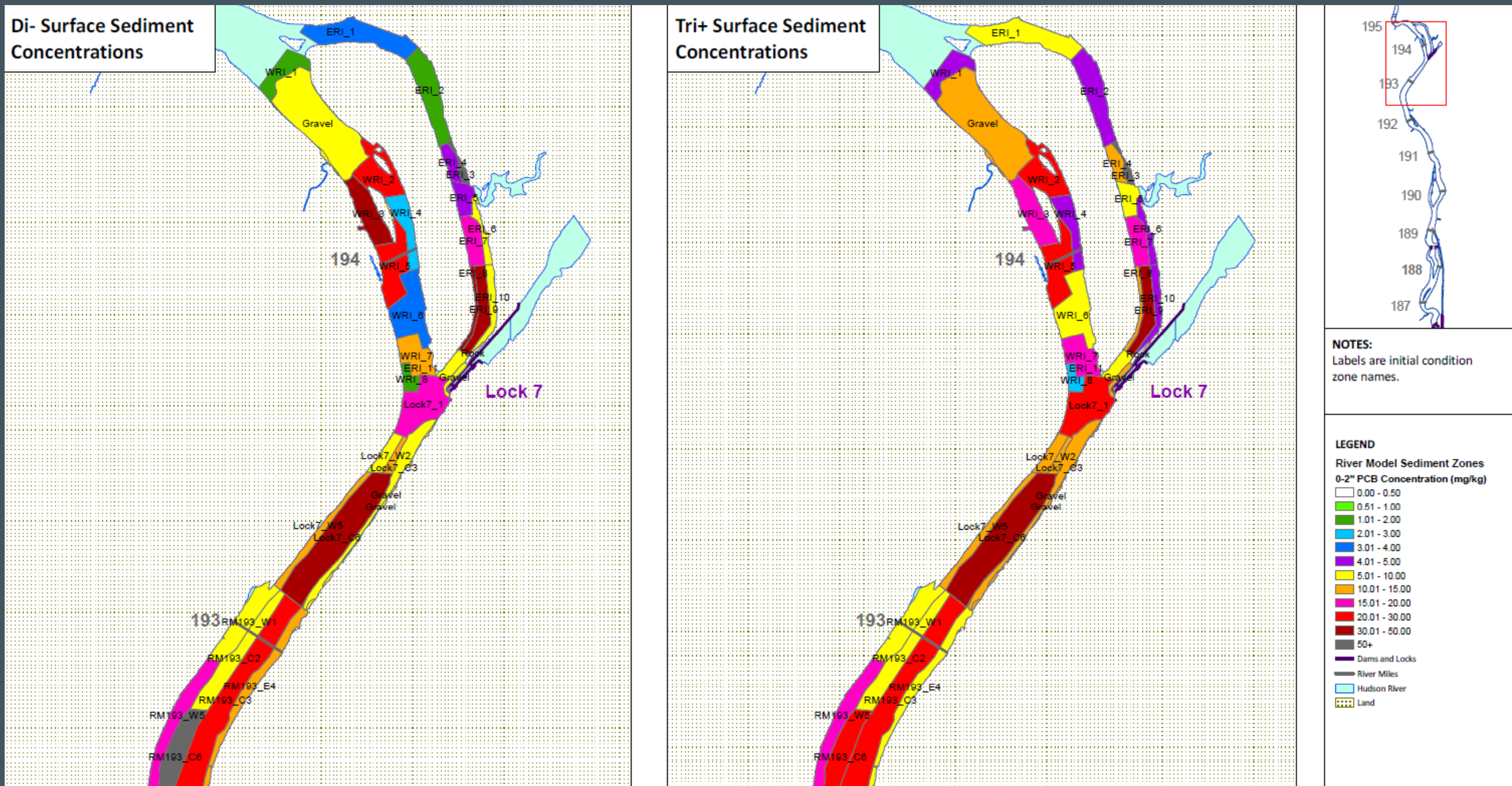
$$Tri + PCB = 0.13[Aroclor1221] + 0.94[Aroclor1242 + Aroclor1254]$$

  - [Di-] = [Total PCB] – [Tri+]
    - Because method was biased high at low [Di-], a 0.75 correction factor of 0.75 was applied to areas with [Di-] less than 133 mg/kg
  - To calculate grid cell PCB concentrations, sediment PCB data was mapped into zones

Initial Conditions

- Sediment PCB Zones
  - In Reach 8 (TIP)
    - Zones based on primary sediment types and spatial patterns of PCB concentrations
  - In Reaches 7 to 1
    - Zones were based on dredge and non-dredge areas
    - Non-dredge areas were further divided by sediment type
  - Model grid cells were assigned the PCB concentrations of the dominant zone within their boundaries

Sediment Zone Initial Conditions



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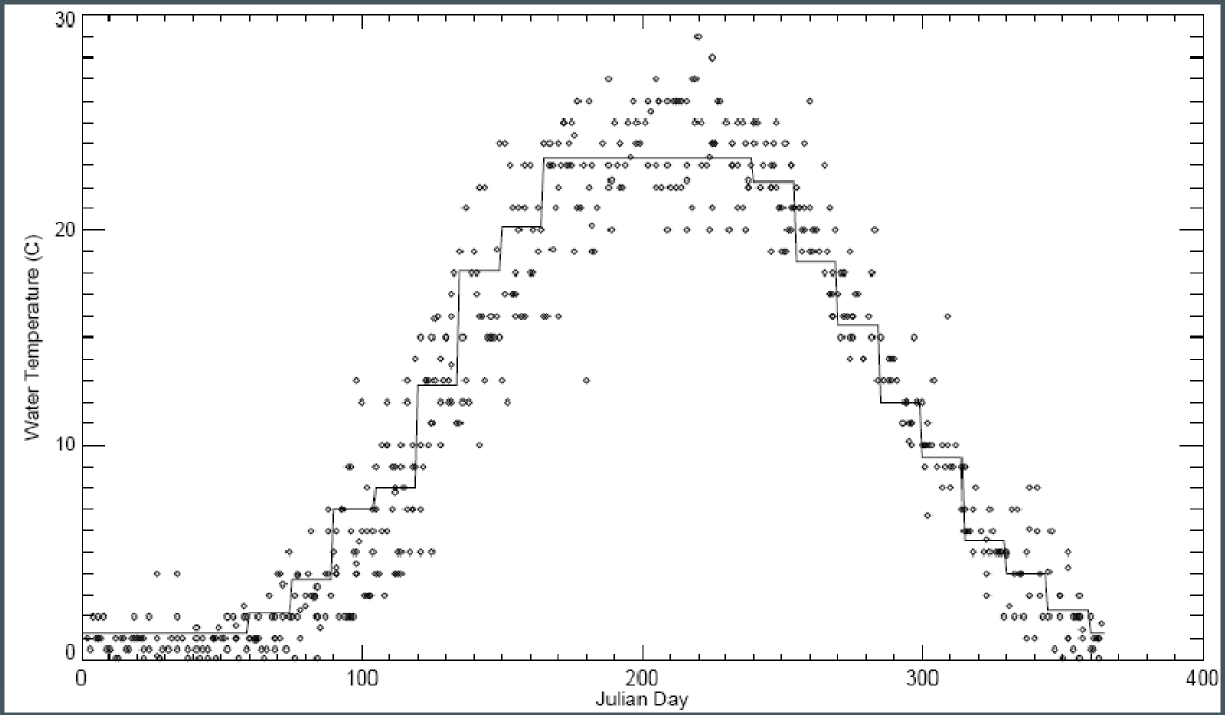
Sediment Characteristics

- 4 size classes as in sediment transport model
- Sediment bed properties
  - Spatial distribution of particle size classes provided by sediment transport model (i.e., bed composition)
  - Reach-specific dry bulk densities as in sediment transport model
  - f_{oc} = 0.026 (cohesive) and 0.021 (non-cohesive)
    - uniform across all sediment size classes
- Suspended sediment properties
  - TSS concentrations from sediment transport model
  - f_{oc} set to 0.1 for all size classes based on BMP data

Temperature Time Series

- Repeating annual temperature cycle based on weekly historical monitoring data
- Used in adjusting temperature dependent variables (partition coefficient, volatilization mass transfer)



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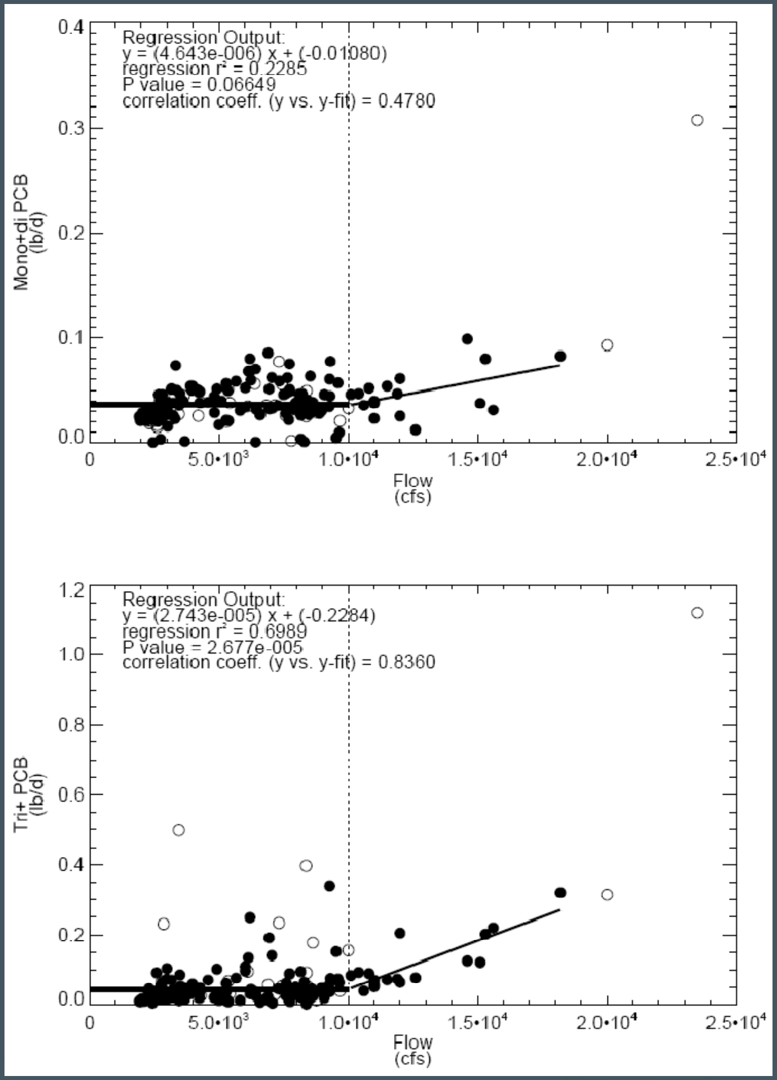
Boundary Conditions for 2004 - 2008 Calibration

- PCB load at upstream boundary of Reach 8
  - Specified *via* load - flow rating curves based on 2004 – 2008 BMP data at Roger's Island
    - On days when data not available
- For downstream reaches, boundary conditions were taken from model predictions in the upstream reach

Boundary Conditions for 2004 - 2008 Calibration

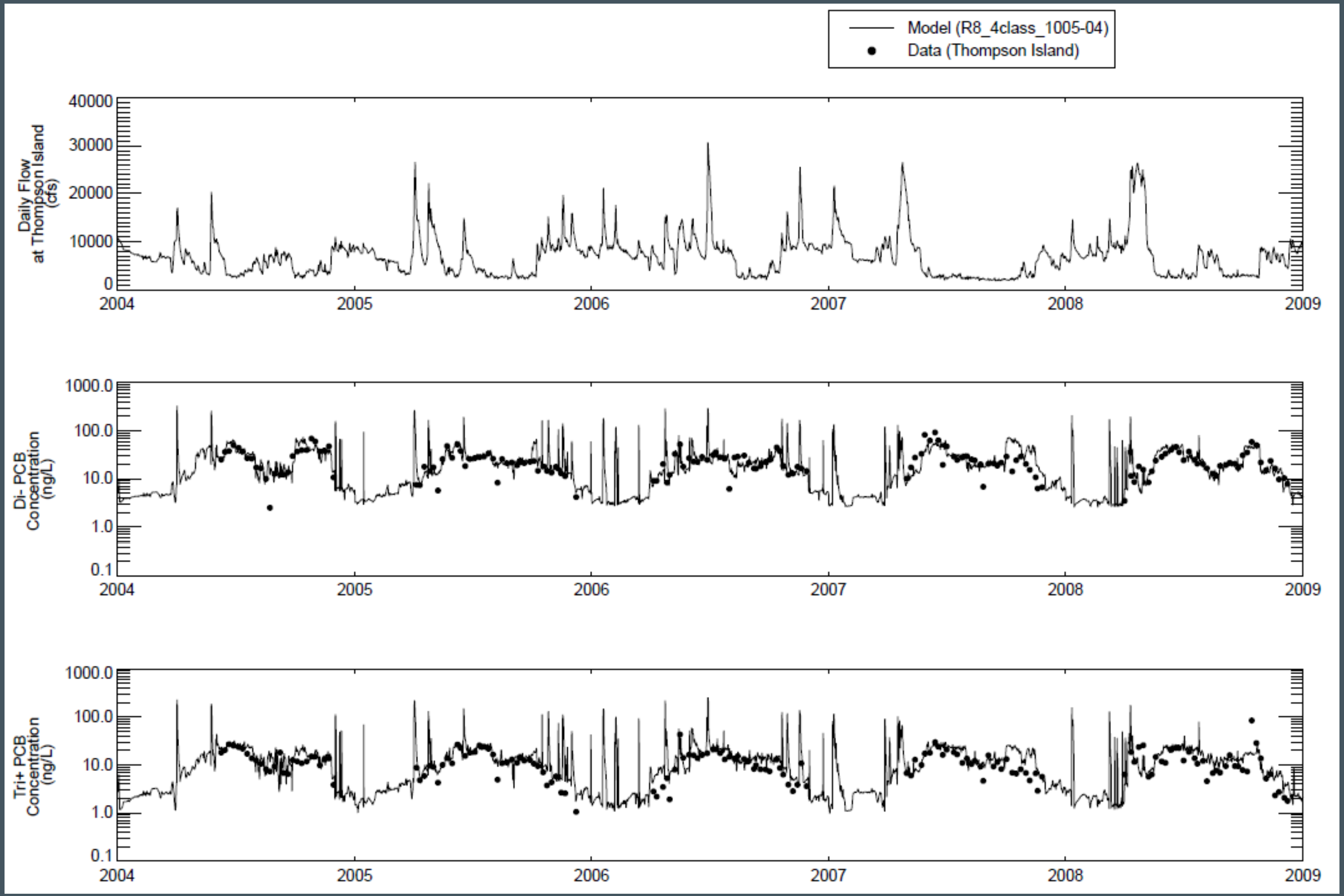
- PCB load-flow rating curves based on BMP data (2004-2008)
  - Measurements from Roger's Island
  - Excludes some anomalous 2008 data



PCB Fate Model Water Column Calibration

- Simulation period: 1/1/2004 to 12/31/2008
- Approach
  - Calibrated to routine (weekly) and high-flow event water column PCB data
  - Calibration adjustments
    - Minor adjustment of sediment-water mass transfer coefficient, k_f
      - Uniform scaling of 1.1 for Di- and 1.3 for Tri+, across all reaches
    - Adjustment to sediment transport model
      - Neglected erosion from the non-cohesive bed at flows less than 10,000 cfs at Fort Edward, i.e., twice the long-term mean
    - Adjustment of chemical erosion flux for coarser particle sizes, to approximate impact of a resistant phase

Calibration: TID PCB Concentrations



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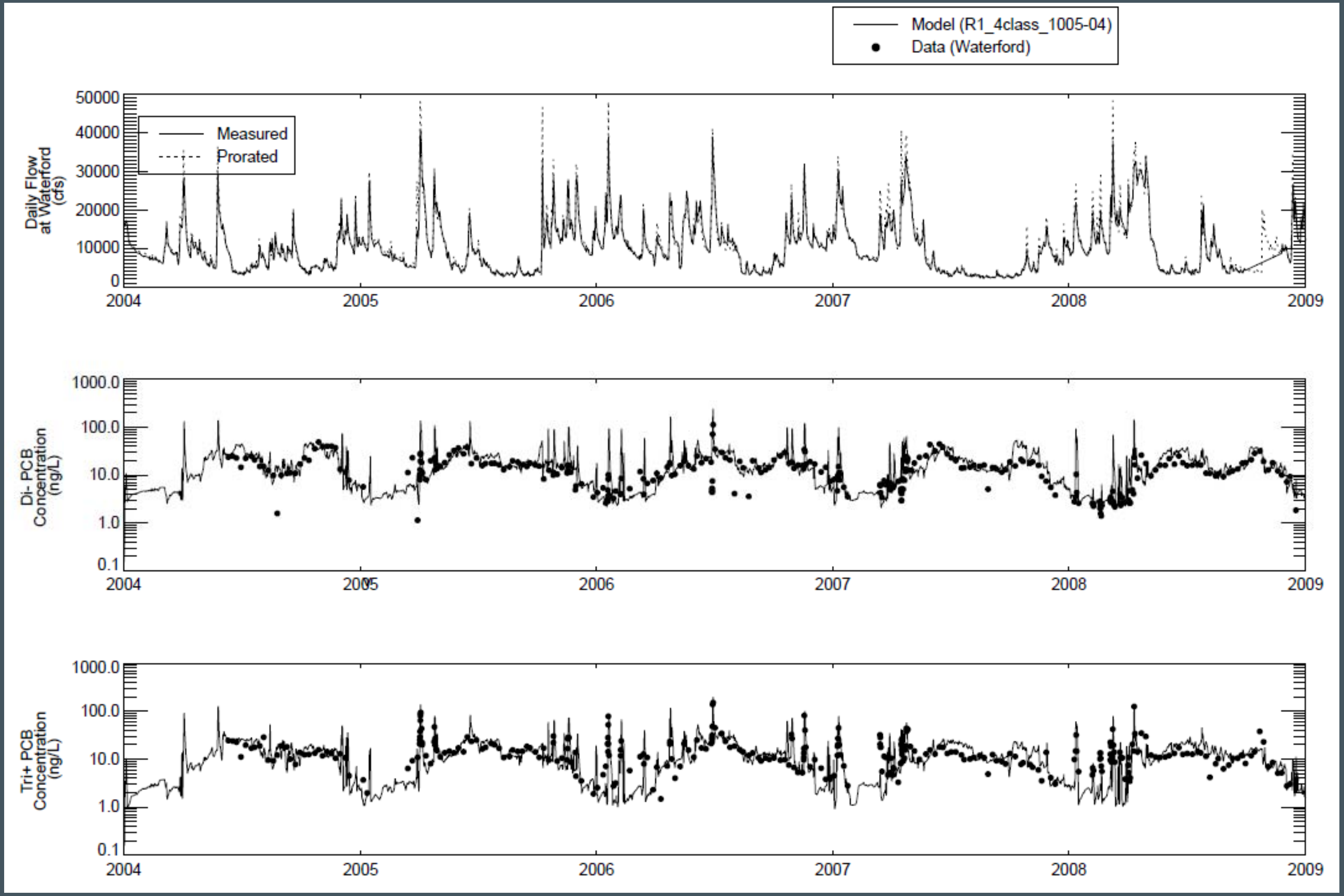
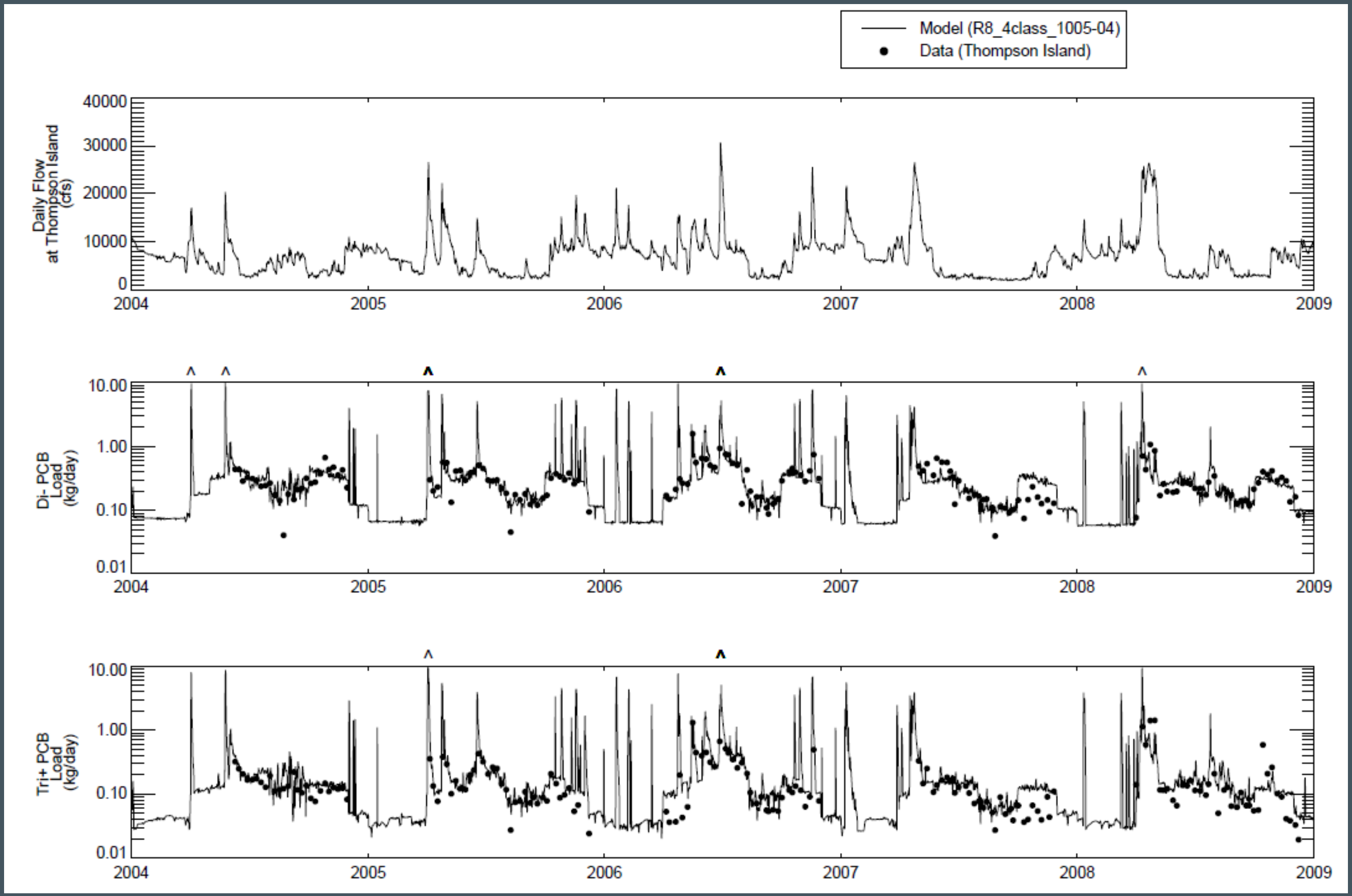
Calibration: Waterford PCB Concentrations



Calibration: TID PCB Load



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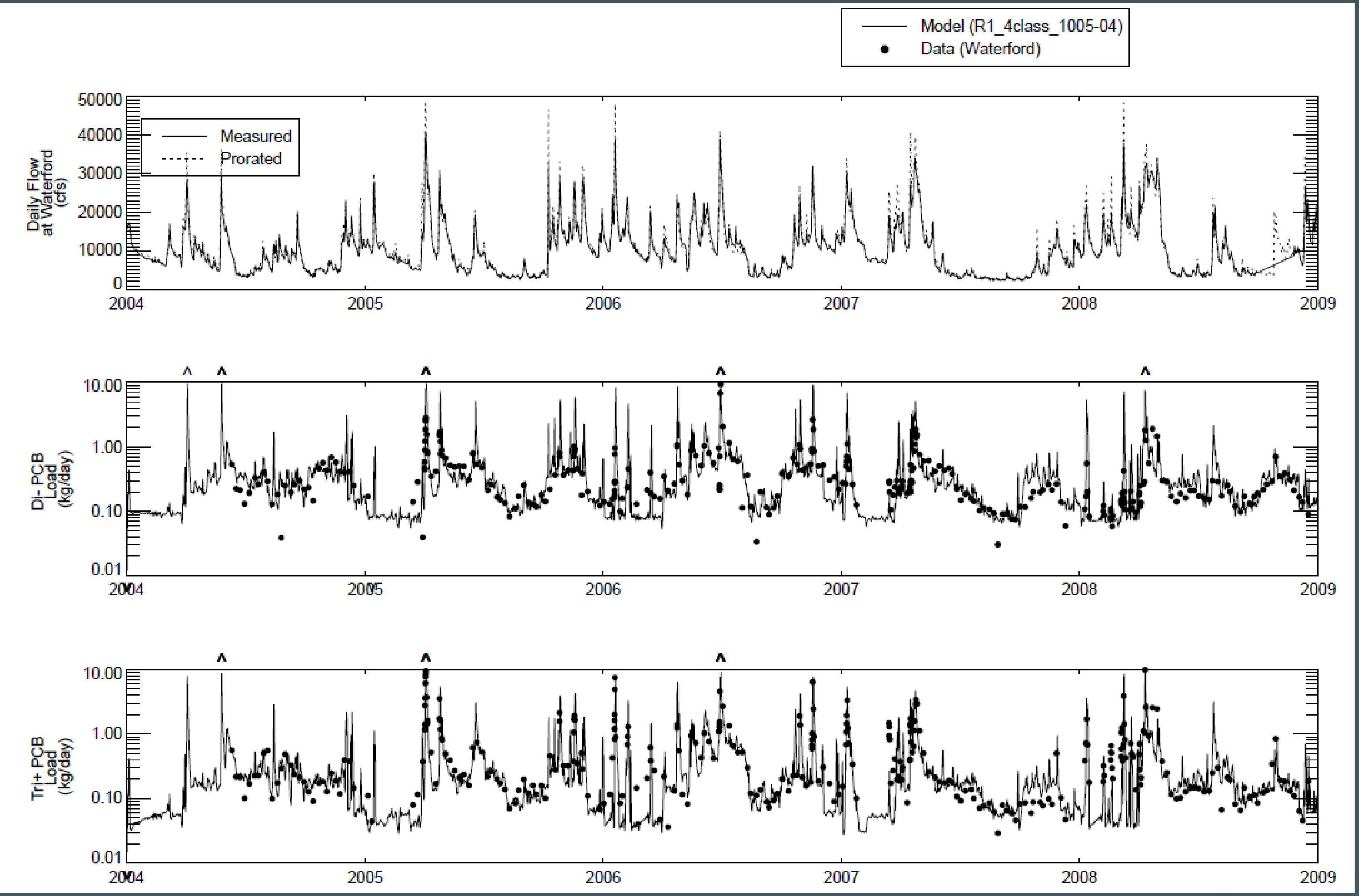
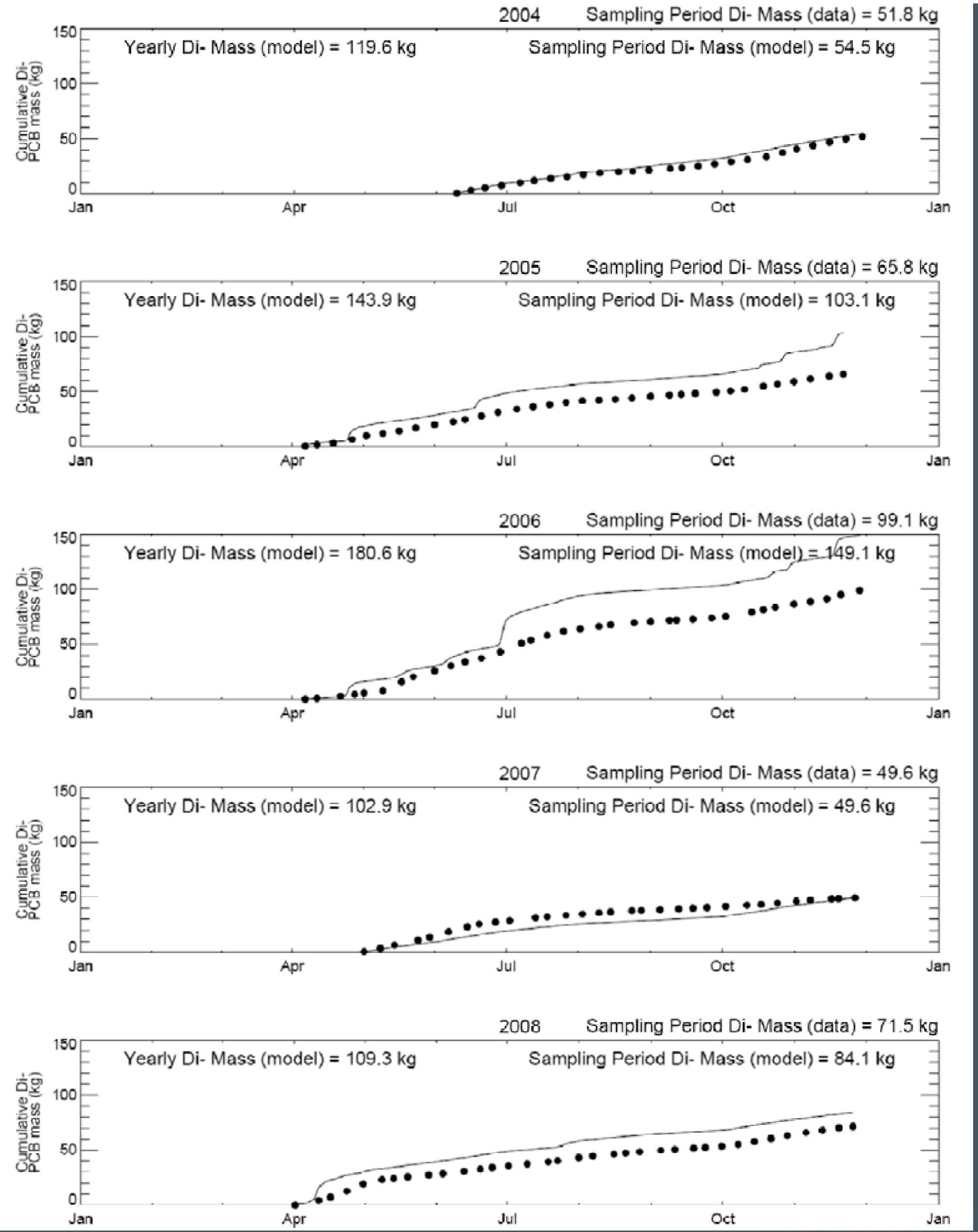
Calibration: Waterford PCB Load



Calibration: TID Cumulative Di- PCB Load



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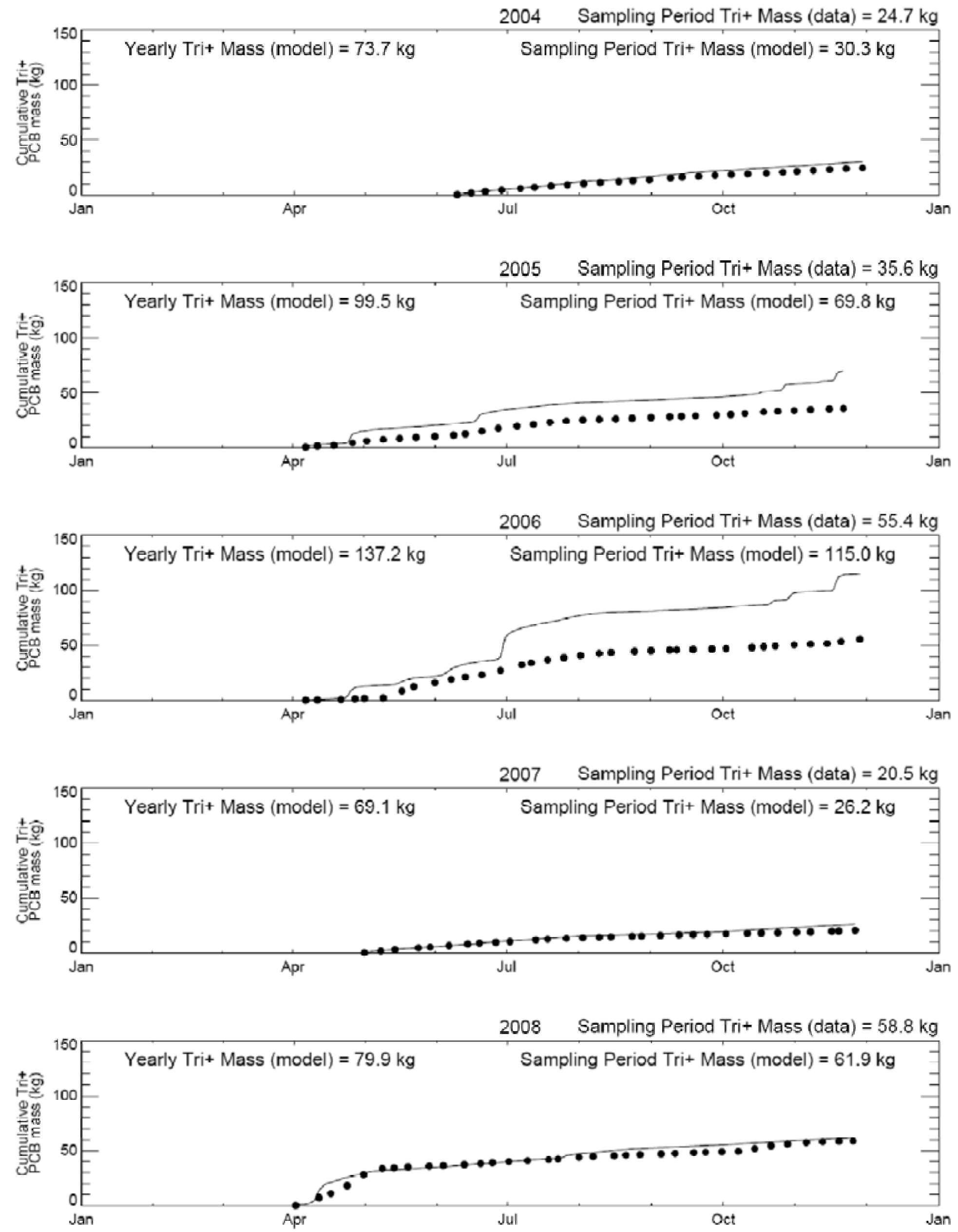
Calibration: TID Cumulative Tri+ PCB Load



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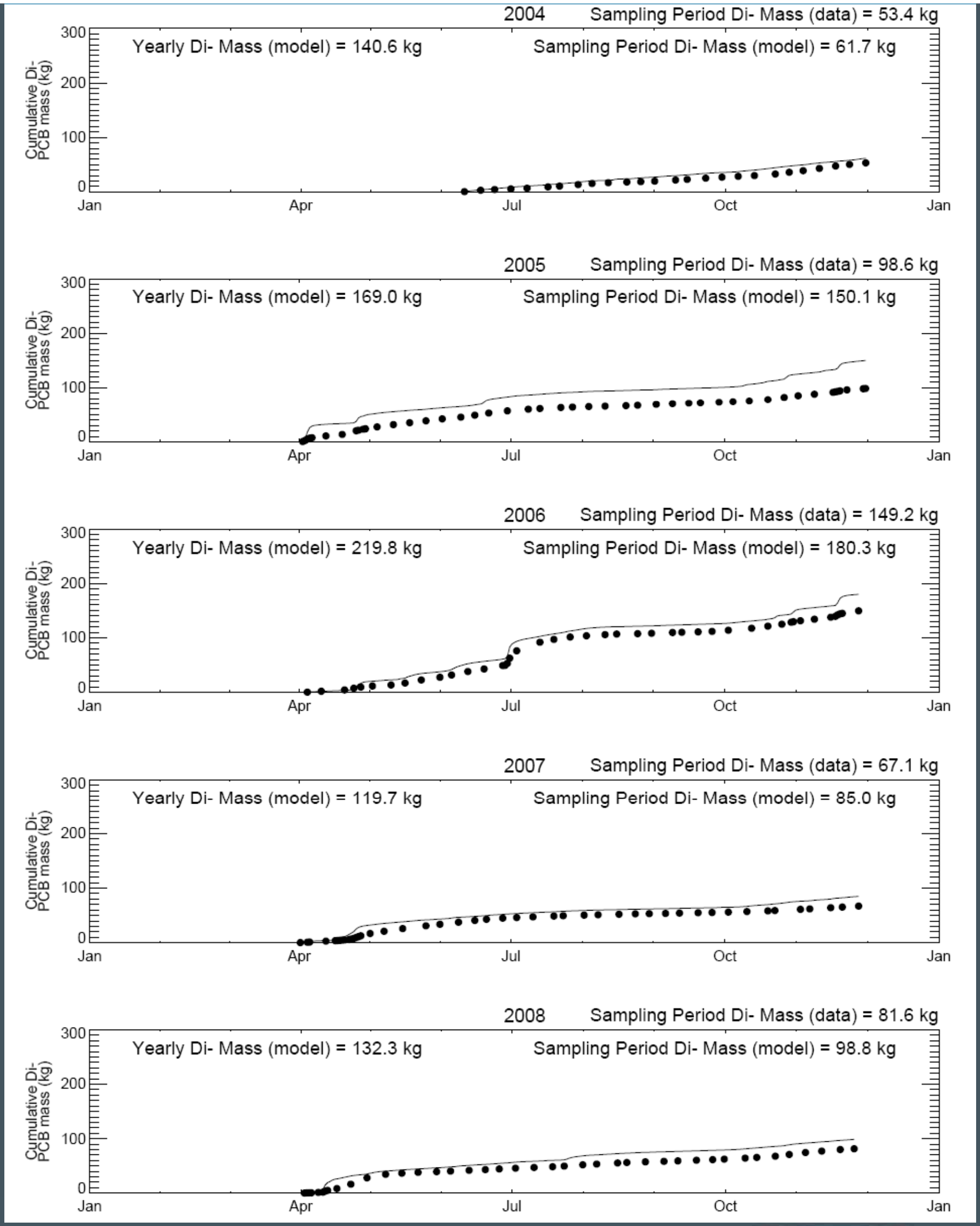
Calibration: Waterford Cumulative Di- PCB Load



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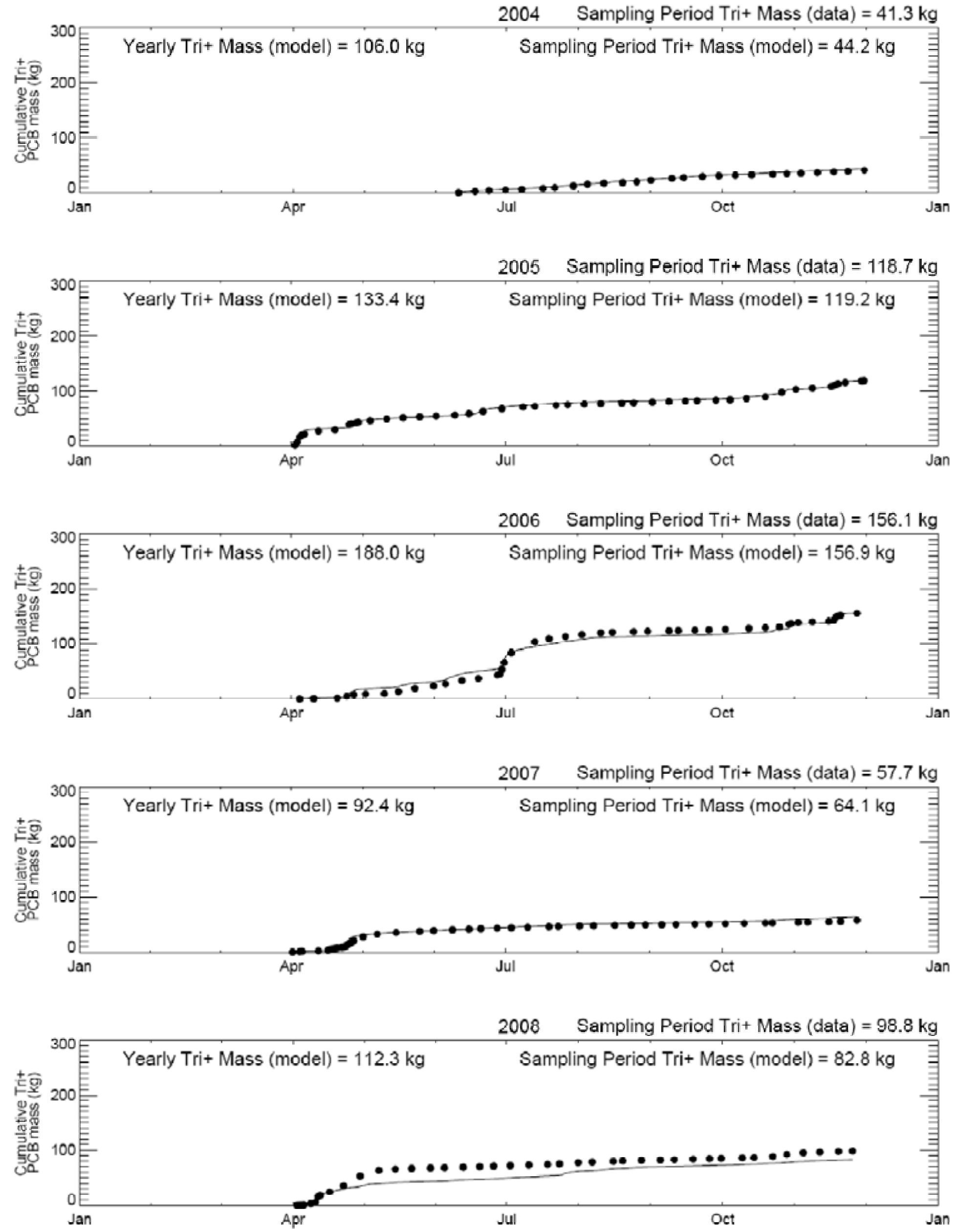
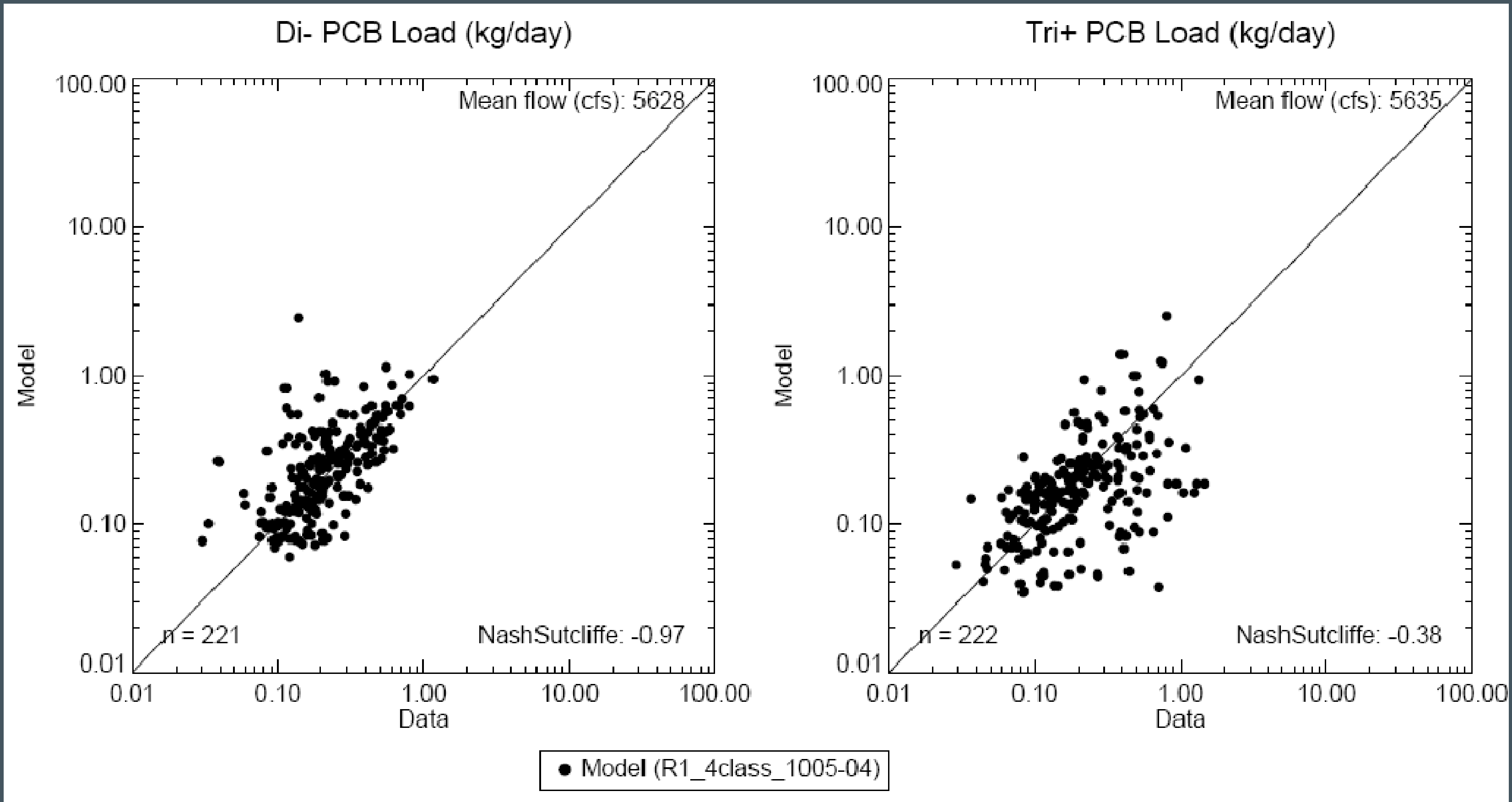
Calibration: Waterford Cumulative Tri+ PCB Load

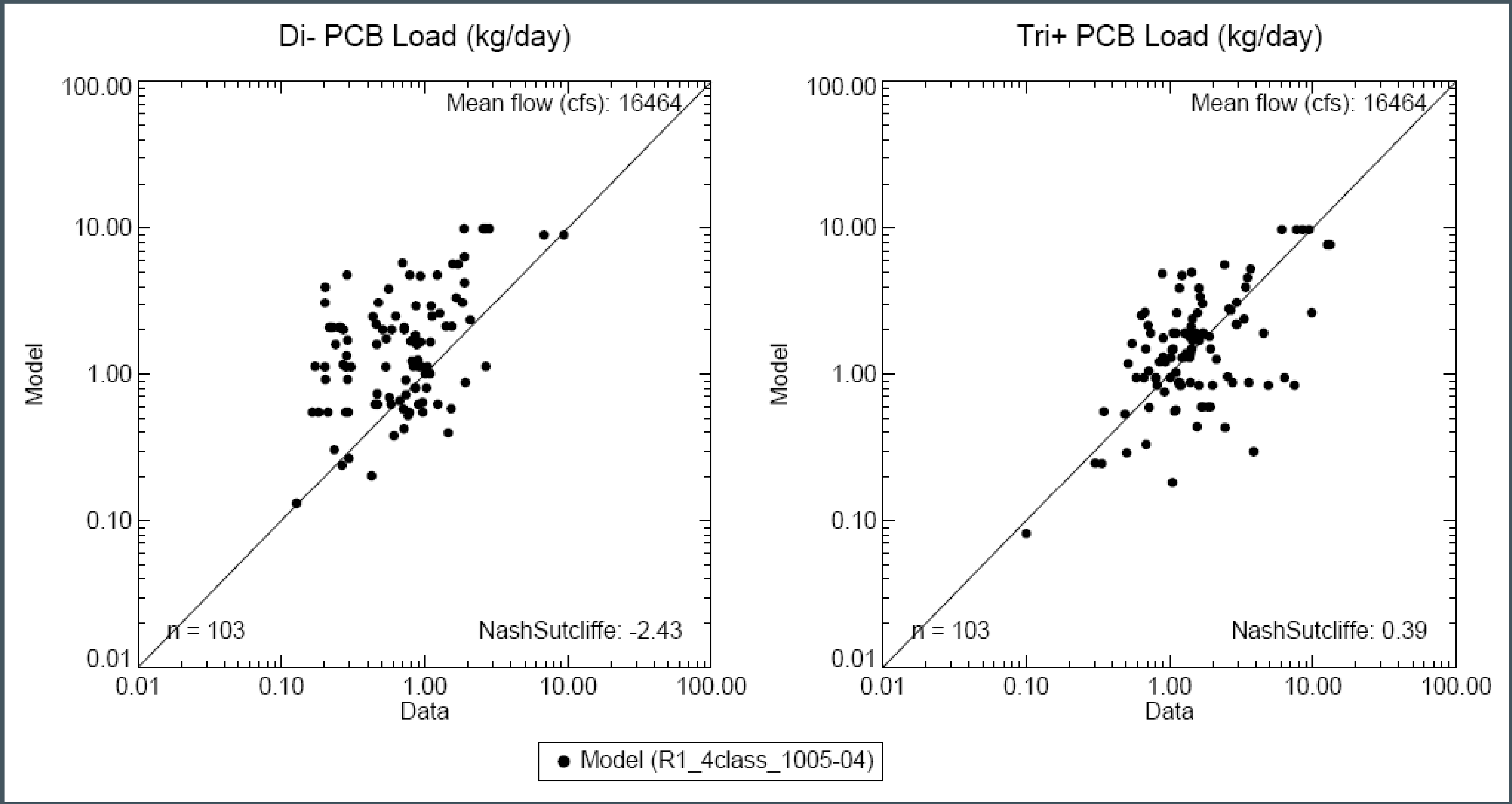


Calibration: Waterford Daily PCB Load (low to moderate flows)



Comparison of days for which Fort Edward flow was less than 10,000 cfs

Calibration: Waterford Daily PCB Load (high flow)



Comparison of days for which Fort Edward flow was greater than 10,000 cfs

PCB Fate Model Calibration Results

- Model to data agreement
  - PCB concentration and load time series at TID, Schuylerville, Stillwater, and Waterford
    - Low- to moderate-flow (< 10,000 cfs at Fort Edward)
      - Generally favorable fit at each location
      - Somewhat better for Tri+ than Di-
    - High-flow conditions (> 10,000 cfs at Fort Edward)
      - Data is sparse for comparison at TID, Schuylerville, and Stillwater
      - At Waterford, favorable agreement
      - Somewhat better for Tri+ than Di-, which shows slight high bias

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PCB Fate Model Calibration Results

- Model to data agreement
  - PCB cumulative loads
    - Generally favorable agreement, although comparisons are complicated by sparse data during high flow events
      - Notably at TID, Schuylerville and Stillwater
      - Causes model to yield higher cumulative load than data in some cases
    - Relative trends in cumulative loading across different stations is consistent with the data
      - See report for more details

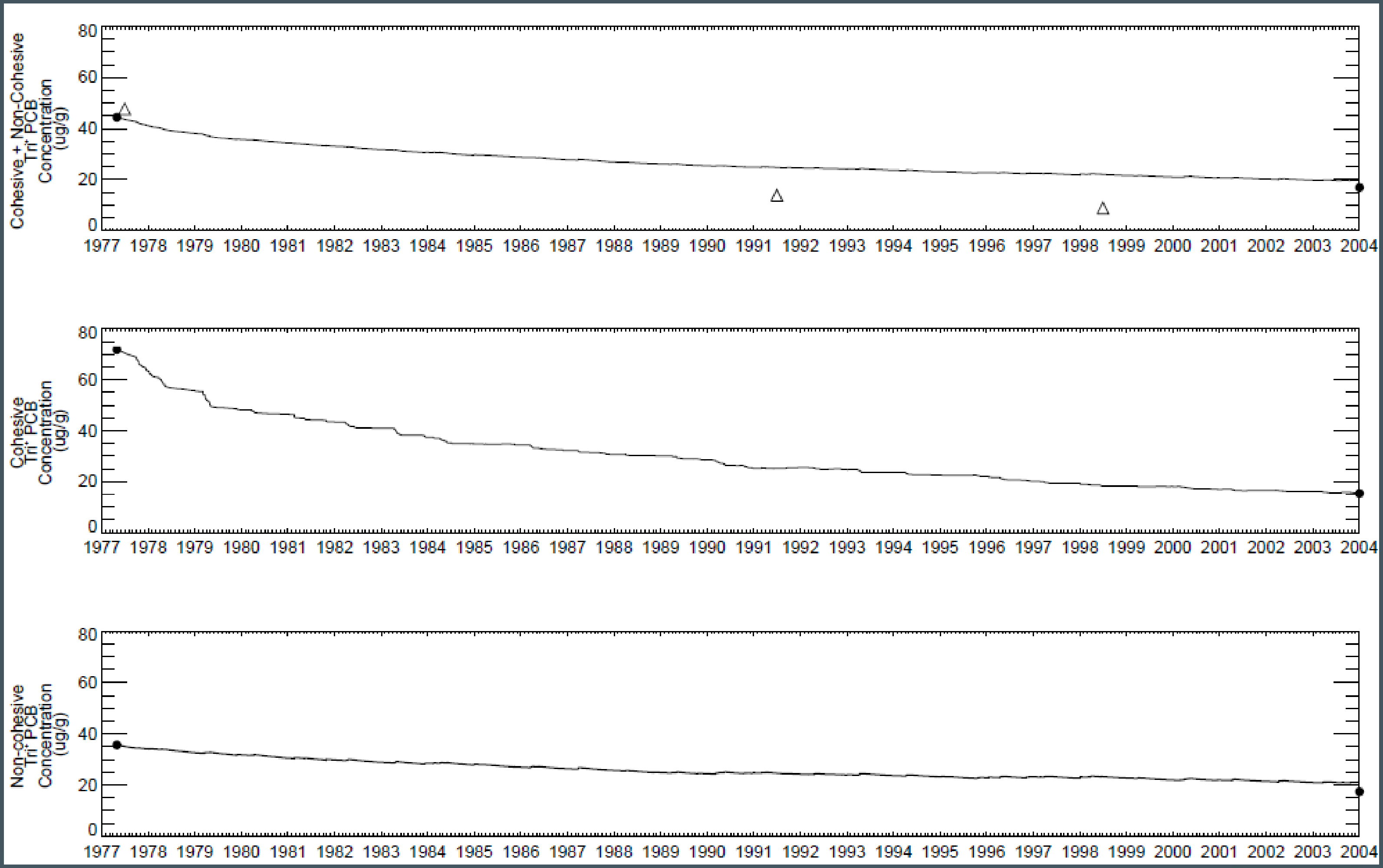
Long-Term Calibration

- Approach
  - 27-year simulation of Tri+ PCBs in Reach 8
    - May 1, 1977 to December 31, 2003
    - Historically, analytical methods only accurately quantified Tri+ PCBs, so Di- PCBs not simulated here due to lack of data
  - Upstream boundary PCB loads
    - 1977 to March 1991: Estimated from USGS data (see QEA 1999 for details)
    - April 1991 through December 2003: Estimated from GE data and USGS flows, linearly interpolating between data gaps

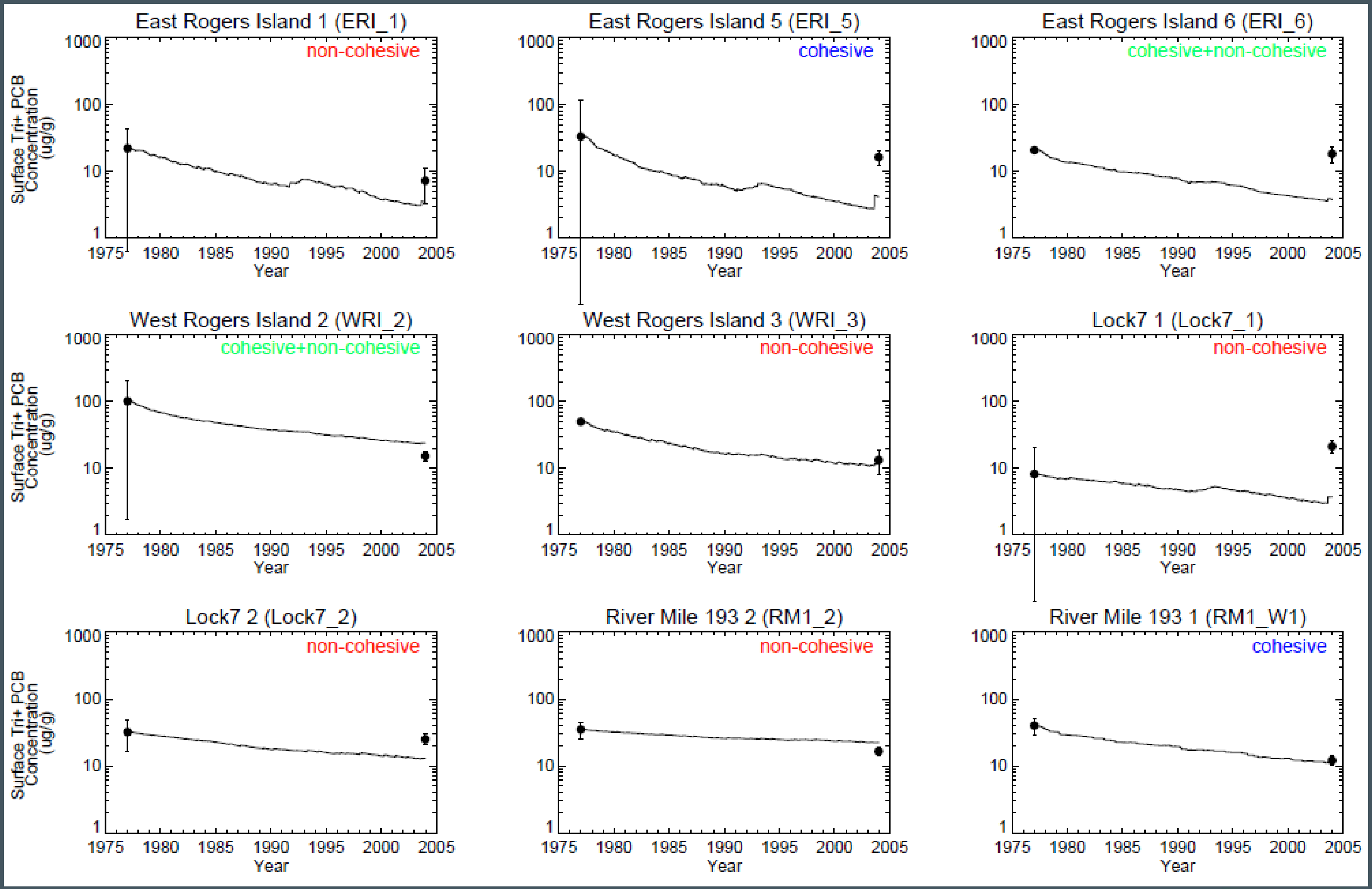
Long-Term Calibration

- Approach (cont'd)
  - Sediment initial conditions
    - Estimated from 1977 NYSDEC sampling program
    - Tri+ PCB concentration profiles estimated from Aroclor measurements in top 12 inches of sediment after binning by zone
  - Model calibration
    - Depth and intensity of bed mixing adjusted
    - Calibrated to rate of decline in surface sediments over 1977 to 2003 period
      - Based on TIP-wide average and zone-by-zone comparisons
      - Select results follow here; see report for full results

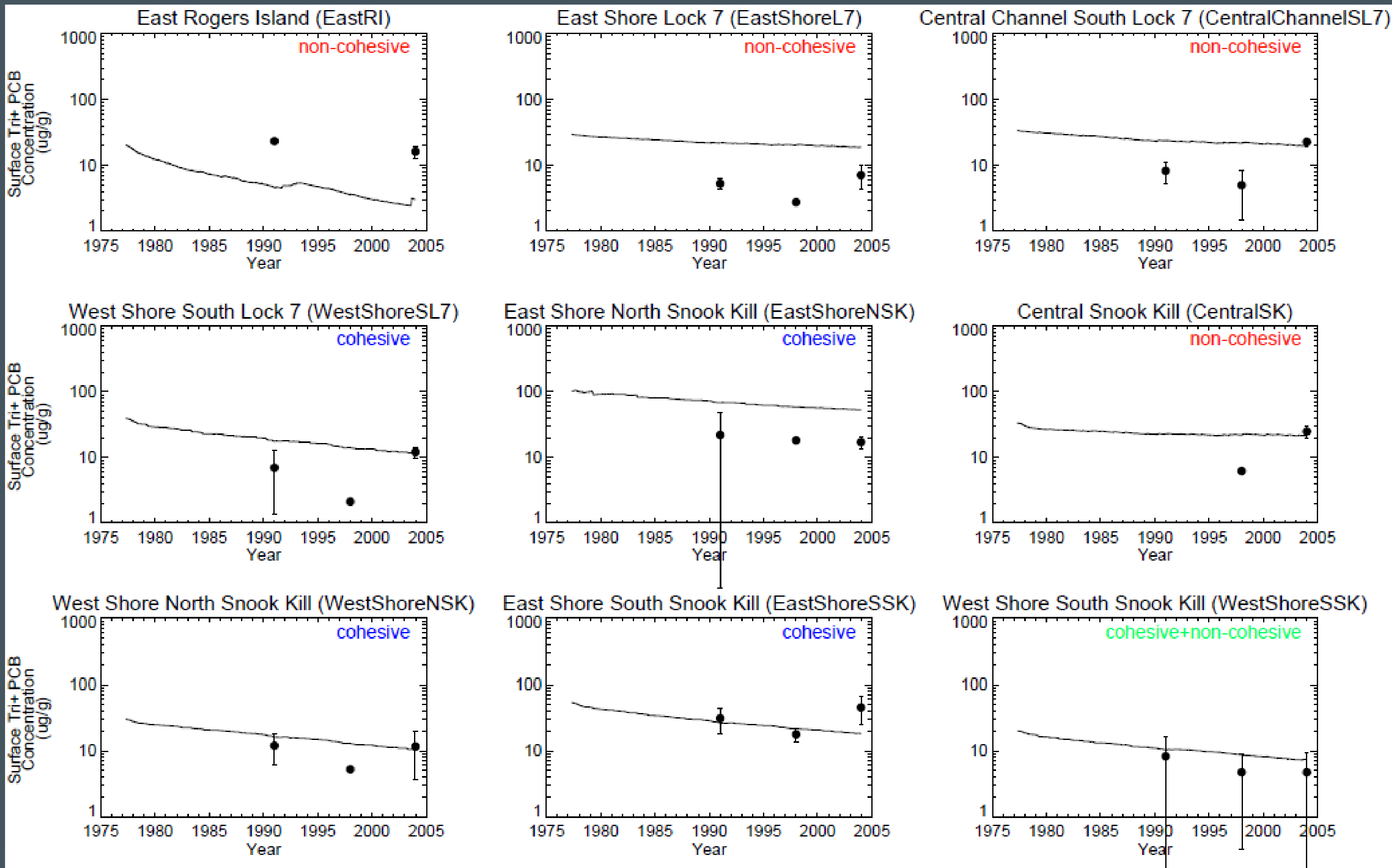
Long-term Calibration Results – Average TIP Surface Sediment Tri+ PCB Concentrations



Long-term Calibration Results – TIP Surface Sediment [Tri+ PCB] in Select 1977 Sediment Zones



Long-term Calibration Results – TIP Surface Sediment [Tri+ PCB] in Select 1990s Sediment Zones



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Long-Term Calibration Results

- Reasonable model-data agreement achieved by setting bed mixing to 2 x 10^{-7} cm^2/s over
  - The top 6 layers (~6”) of cohesive sediment bed
  - The top 2 layers (~2”) of non-cohesive sediment bed
- Note uncertainties in data sets
  - TIP-wide averages are sensitive to data coverage
  - SSAP data set had 3,000+ sediment cores in TIP, but prior sampling events had poorer coverage
    - For example, 1990’s TIP-wide averages are highly uncertain
- In general, model tends to under-predict decline of non-cohesive sediment concentrations, and therefore under-predict overall decline

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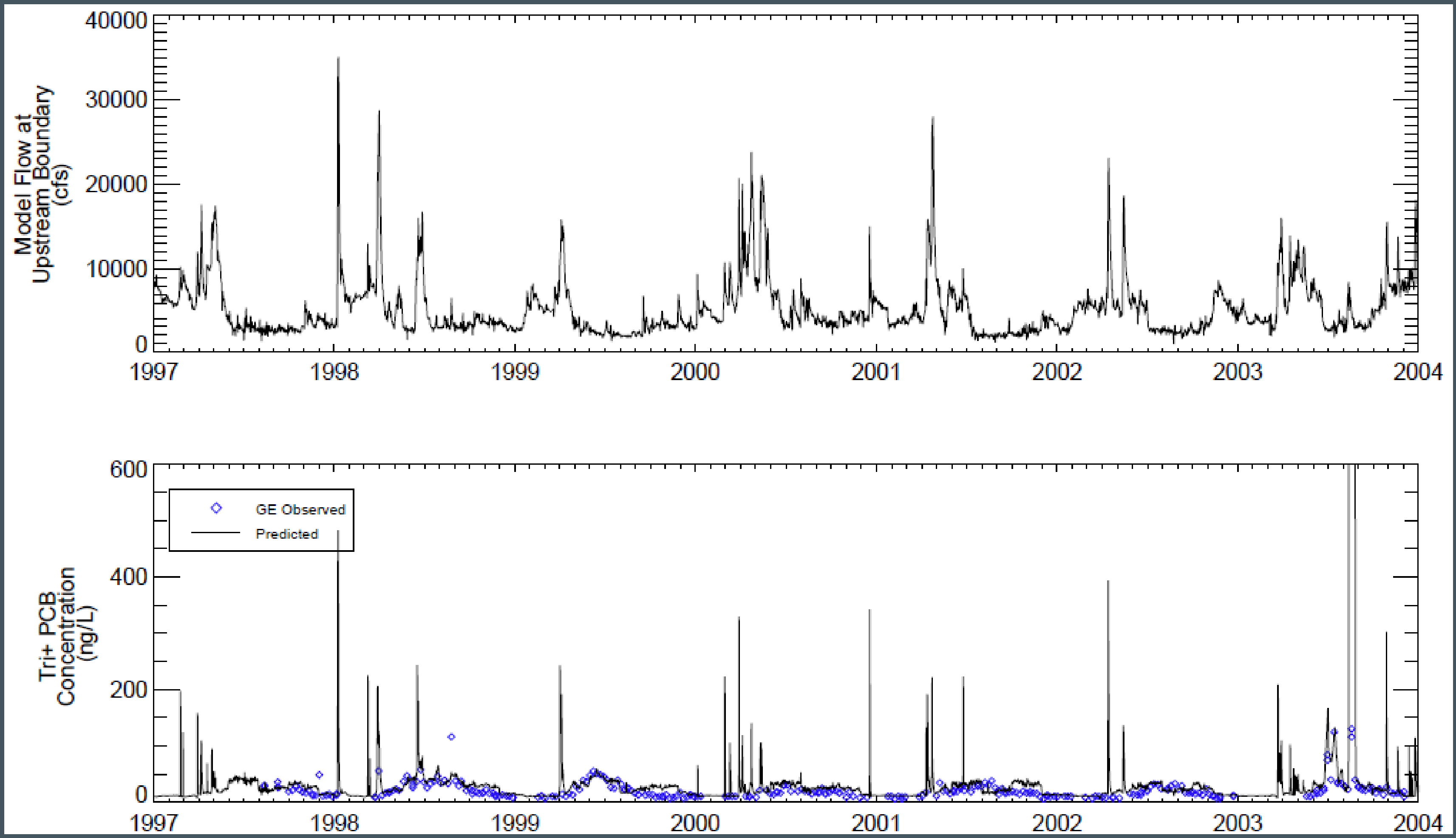
Long-Term Calibration Results

- Predicted water column Tri+ concentrations were also compared to measured data
  - October 1997 through 2003 only (pre-1997 data not representative of the cross-sectional average)
- Model generally reproduces seasonal trend in Tri+ PCB concentrations at TID, tending to slightly over-predict absolute concentrations
  - Consistent with an under-prediction of sediment concentration decline
  - Serves as a reasonable validation of water column calibration parameters

Long-term Calibration Results – TIP Water Column Tri+ PCB Concentrations



PCB Fate Model – Calibration Conclusions

- Water column calibration
  - Taken as a whole, calibration results indicate favorable model-data agreement across multiple metrics
    - Including PCB load predictions across a range of flow regimes and stations
- Sediment bed calibration
  - Calibration results indicate that the large-scale trend of declining surface sediment concentrations in Reach 8 is captured, though perhaps under-predicted
  - Zone-by-zone comparisons are variable but generally reasonable, given uncertainty in both data-based concentration estimates as well as model parameters

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PCB Fate Model – Ongoing work

- Sensitivity analysis on model calibration parameters and assumptions
- Application of model to simulate 2009 dredging
  - Evaluating model performance in detail and possible refinements to the approach taken to date
  - To be covered Thursday afternoon, 7/15
- Application of model to simulate Phase 2 dredging
  - To be covered Thursday afternoon, 7/15

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